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Singlet and Triplet Nitrenes. III. The Addition of Carbethoxynitrene to 1,3-Dienes

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Carbethoxynitrene adds to the double bonds of isoprene to give two isomeric aziridines. At high isoprene concentrations, where the singlet nitrene predominates, the adducts are formed in approximately equal amounts. At low isoprene concentrations, where much of the nitrene has time to go to the triplet state, the methyl-substituted double bond is preferred. No 1,4-addition product could be detected. The addition of the nitrene to cyclopentadiene and 1,3-cyclohexadiene also did not give 1,4-addition products, but only aziridines and substances derived from them, such as oxazolines. The N-carbethoxy-2-methyl-2-vinylaziridine underwent a new thermal rearrangement to give N-carbethoxy-3-methyl-3-pyrroline.

The addition of carbethoxynitrene to *cis*- and *trans*-4-methylpent-2-ene conforms to a model[2,3] in which singlet carbethoxynitrene changes to triplet carbethoxynitrene in competition with the addition of the singlet to the olefin. Furthermore, both the singlet and the triplet behave in accord with a rule set forth by Skell[4]—the singlet adds stereospecifically and the triplet completely nonstereospecifically. Consequently, the over-all degree of stereospecificity depends on the olefin concentration. The earlier papers[2,3] related this dependence quantitatively to the change of singlet to triplet and to the relative abundance of the two. Recent work by Nozaki[5] and by Beckwith[6] further confirms the validity of our model.

Investigation of the addition of carbethoxynitrene to 1,3-dienes seemed to promise two results: possible 1,4 cycloaddition to form pyrroline derivatives and information on the relative reactivity of differently substituted double bonds in appropriately chosen olefins. The study of relative reactivities is of special interest in comparing nitrenes with carbenes. Skell[7] has shown that triplet carbenes display relative reactivities toward olefins that parallel those of free radicals, while the relative reactivities of singlet carbenes depend but little on olefin structure.

We chose isoprene as the subject of a detailed study. If Skell's rule for the relative reactivities of singlets and triplets holds for carbethoxynitrene, the fraction of addition to the methyl-substituted double bond of isoprene should increase with decreasing isoprene concentration, since at low olefin concentration more of the nitrene will have time to change to the triplet state. Also, isoprene was thought to be a good candidate for 1,4 addition, since a significant fraction of its molecules is in the *s-cis* conformation, although the *s-trans* conformation predominates.[8] The first step of a radical addition is expected to freeze the conformation of isoprene by forming an allylic radical, as shown in Scheme I. Hoping to find 1,4 cycloaddition, we also investigated the reactions of carbethoxynitrene, in dilute solution, with cyclopentadiene and 1,3-cyclohexadiene. Before discussing our results, it seems appropriate to review briefly the pertinent literature.

Cyclopentene was found in gas phase additions of methylene to 1,3-butadiene and its formation has been ascribed both to genuine 1,4 addition[9-11] and to rearrangement of the primary product, thermally excited vinylcyclopropane.[12,13] Two cases of 1,4 cycloaddition of nitrenes to 1,3-dienes have been reported. Appel[14] found traces of pyrroline when he decomposed the anion of hydroxylamine-O-sulfonic acid in the presence of

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(2) J. S. McConaghy and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967).

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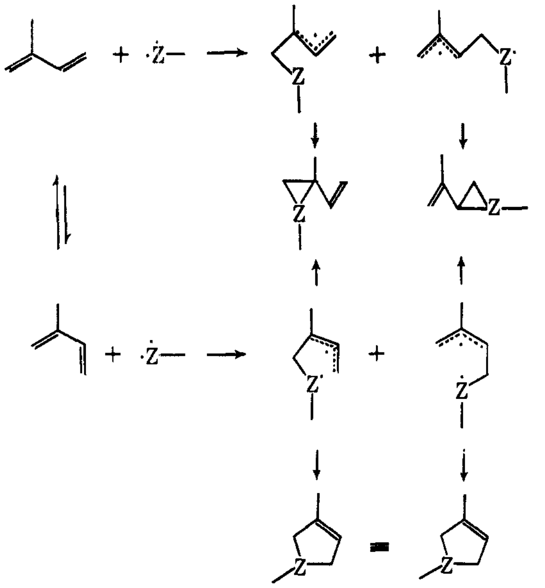
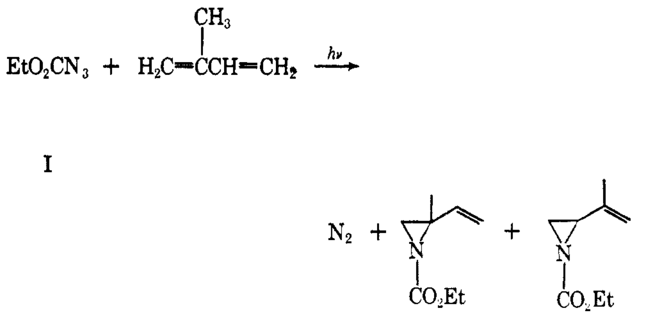
Scheme I



1,3-butadiene. However, it is not certain that the pyrroline was formed by direct 1,4 addition of NH to butadiene. Even a process not involving NH at all seems possible.[15] Cyanonitrene, presumably in its triplet state, adds to cyclooctatetraene in a 1,4 fashion, while the singlet gives 1,2 addition.[16] Carbethoxynitrene undergoes only 1,2 addition with 1,3-butadiene and cyclooctatetraene;[17] 1,4 adducts could not be detected. Additions to isoprene of dichlorocarbene[18–21] and dibromocarbene[21] gave only 1,2 adducts, with a strong preference of addition to the methyl-substituted double bond. The dihalocarbenes used might not have been free carbenes, however. Reaction of isoprene with diazoacetic ester at elevated temperatures (without catalyst) gave a 63% yield of the cyclopropane derived from addition to the less substituted double bond,[22] while copper-catalyzed decomposition of diazoacetic ester in isoprene gave the product of addition to the methyl-substituted double bond as the only monoaddition product.[23]

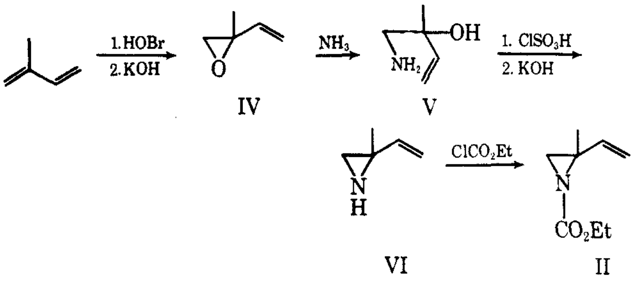
Results

Isoprene.—The photolytic decomposition of ethyl azidoformate[24] in isoprene gave a mixture of two products in 95% yield. Separated by glpc, they were identified as N-carbethoxy-2-methyl-2-vinylaziridine (II) and N-carbethoxy-2-isopropenylaziridine (III), the two 1,2-addition products. Neither the 1,4-addition product nor CH insertion products were found. The products II and III were identified by their elemental analyses, infrared and nmr spectra, and comparison with authentic samples. Compound II was synthesized from the known oxirane IV[25] according to Scheme II. The structure of the intermediate V (4-amino-3-hydroxy-3-methylbutene-1) was confirmed by its nmr spectrum. The methylene signal appears at δ 2.50, rather than at 3.7 as one would expect for the methylene signal of the isomeric 3-amino-4-hydroxy-3-methylbutene-1. Apparently, the ammonia attacks the less hindered carbon in IV. Other vinylaziridines have recently been synthesized[26] by the standard method[27] employed here. The aziridine III was reduced to VII, which was synthesized by Hassner's method[28] from 3-methylbutene-1.

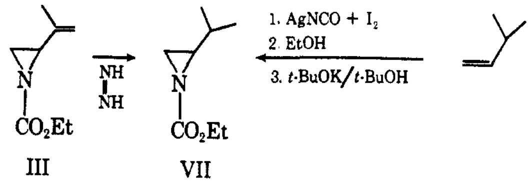


I II III

Scheme II



IV V VI II



III VII

Carbethoxynitrene was also generated by α elimination[29] and added to isoprene. The yield of compounds containing the isoprene moiety was 60%. Besides compounds II and III, a new isomer VIII was found. This new isomer could also be produced by injection of pure II onto a vpc column which had been used before to separate the reaction mixture from the α-elimination reaction. Apparently, some constituent of this reaction mixture remained on the column or in the injector block and catalyzed the conversion of II to VIII. The aziridine III did not isomerize under these conditions. The infrared spectrum of VIII is similar to that of the oxazoline IX[29] and the nmr spectrum also was compati-

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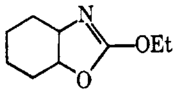
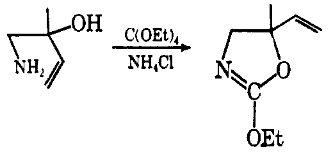


IX



V VIII

ble with the oxazoline structure, which was confirmed by independent synthesis from V. Under the vpc conditions used, injection of II gave a mixture of II and VIII very similar to that produced in the α-elimination experiments. It seems, therefore, that little or no VIII is a primary reaction product and that VIII is formed at the expense of II.

Dilution Experiments.—We had established earlier[2,3] that both singlet and triplet carbethoxynitrene add to double bonds, but with different stereospecificity. This led us to investigate the effect of isoprene concentration on the distribution of II and III (or, for reasons of analytical procedure, of VIII and III) in the product mixture. Table I shows the results of photolyses of ethyl azoidoformate in isoprene-dichloromethane mixtures, employing a 1:10 molar ratio of azide to olefin. The same ratio was employed in the α-elimination runs. In these, it proved most practical to carry out the product analysis under vpc conditions that isomerized all II to VIII. The results are given in Table II. In both series, the trend toward increased formation of II (the addition product to the more substituted double bond) is clear. The yields, especially in the photolysis runs, are quite high, even at low olefin concentrations.

TABLE I

DISTRIBUTION OF II AND III IN PHOTOLYSES OF ETHYL AZIDOFORMATE AT VARIOUS ISOPRENE CONCENTRATIONS

Mole % of isoprene in CH_2Cl_2	Yield of aziridines, %	Yield of ethyl carbamate, %	Ratio of II:III
100	95 ± 2	0	1.17 ± 0.05
30	86 ± 3	0	1.21 ± 0.03
2.5	87 ± 1	2	1.45 ± 0.02
0.5	85 ± 2	6	2.13 ± 0.05

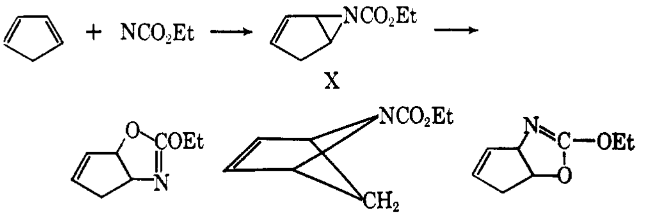
TABLE II

DISTRIBUTION OF VIII AND III FROM THE ADDITION OF CARBETHOXYNITRENE TO ISOPRENE. α-ELIMINATION RUNS

Mole % of isoprene in CH_2Cl_2	Yield of VIII + III, %	Ratio of VIII:III
30	60	1.08 ± 0.03
10	45	1.20 ± 0.03
2.5	43	1.35 ± 0.03
0.7	43	1.52 ± 0.05

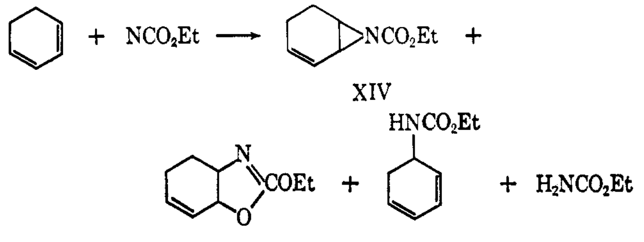
The relatively small effect of structural changes on the reactivity of olefins toward singlet carbenes[7] prompted us to compare, in an approximate fashion, the reactivities of isoprene and cyclohexene toward singlet carbethoxynitrene. In a mixture of 2 moles of cyclohexene per mole of isoprene, the photolysis of ethyl azidoformate gave about 1.6 times as much product from the isoprene as from the cyclohexene. The same ratio was obtained at 10 mole % olefin concentration in dichloromethane. The figure is based on the assumption that the hot wire detector of our vpc apparatus responded equally to the three products. Our value is thus only approximate, but it seems safe to say that isoprene is no more than about twice as reactive (per double bond) as is cyclohexene in its reaction with singlet carbethoxynitrene.

Cyclopentadiene.—Carbethoxynitrene was generated by α elimination in dichloromethane solution, containing 13 mole % of cyclopentadiene. Volatile products were obtained in 30% yield. Their separation by vpc showed only two components, which were identified by their infrared and nmr spectra as the 1,2 adduct X and its isomerization product, the oxazoline XI. None of the 1,4-additon product XII was found and nmr spectra of the crude mixture of volatile products did not show extra signals attributable to XII. Because of its symmetry, XII would have a nmr spectrum distinctly different from those of X and XI and a few per cent of XII should have easily been detected in the reaction mixture. The aziridine X could be converted into XI by injecting it into a vpc apparatus that had previously been used to separate reaction mixture from α-elimination runs. Thus, it seems to be a secondary product. The oxazoline is formulated as XI not as the isomer XIII, in analogy with the independently established structure of VIII, in which the oxygen is also connected to the allylic carbon. The rearrangement seems to correspond to the acid-catalyzed formation of oxazolines from N-acylaziridines, rather than to the one induced by nucleophilic catalysts.[30]



XI XII XIII

Cyclohexadiene-1,3.—Reaction of carbethoxynitrene, made by α-elimination in a dichloromethane solution containing 4 mole % of cyclohexadiene-1,3, gave four volatile products in 20% yield. One was identified as ethyl carbamate (a common side product in α-elimination runs) by its infrared spectrum and vpc retention time. The other three were identified by their nmr and infrared spectra (see the Experimental Section) as the 1,2 adduct, 7-carbethoxy-7-azabicyclo[4.1.0]hept-1-ene (XIV), as the oxazoline XV derived from XIV, and as 5-carbethoxyamidocyclohexadiene-1,3 (XVI). The amide XVI could perhaps be the allylic insertion product (*cf.* ref 24 and 29), but it could also be formed by a rearrangement of XIV, restoring the diene system. The latter origin of XVI is made likely by its abun-



XV XVI

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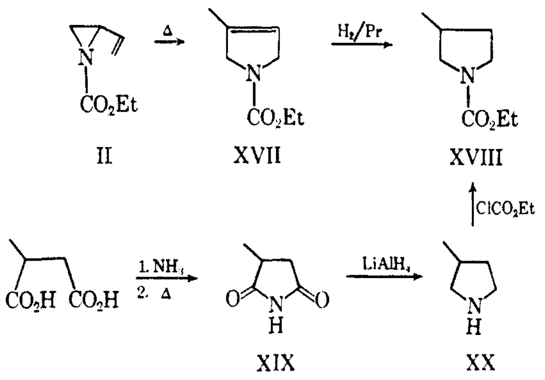
dance. Assuming equal vpc detector response for the four compounds, the product mixture consists of 18% of ethyl carbamate, 41% of XIV and XV, and 41% of XVI. From the experience with isoprene and with cyclohexene, one would expect much less allylic insertion to take place. It seems possible that much of the product XVI is formed from vibrationally excited XIV, immediately after formation of the latter.

A Vinylaziridine–Pyrroline Rearrangement.—N-Carbethoxy-2-methyl-2-vinylaziridine (II) isomerized when subjected to gas chromatography at column temperatures of 100° or above, giving N-carbethoxy-3-methyl-3-pyrroline (XVII). Its structure was deduced from its spectral data and confirmed by reducing XVII to the corresponding pyrrolidine, which was synthesized from 3-methylsuccinic acid according to Scheme III.

SCHEME III



A similar but iodide-catalyzed vinylaziridine–pyrroline rearrangement has recently been reported.[31] The carbon analog, the vinylcyclopropane–cyclopentene rearrangement, is well known.[32]

Discussion

Inspection of Table II shows that the relative amount of II, the product of addition to the methyl-substituted double bond, increases with decreasing olefin concentration. This is the effect expected. Addition of the triplet nitrene should involve diradical intermediates, of which the one leading to II would be better stabilized and presumably be formed *via* a better stabilized transition state. Table II also shows very little discrimination between the two double bonds at high isoprene concentration (when most of the nitrene is present as the singlet). Assuming no discrimination by the singlet, we can write a simplified kinetic scheme (Scheme IV) in which the selectivity factor for the triplet nitrene is called m. From the scheme, and using a steady-state approximation for the concentration of the triplet, eq 1 can be deduced.

SCHEME IV

$$\begin{tikzcd}
\text{singlet nitrene} \arrow[d, "k_s"] \arrow[dr, "k_s"] \arrow[rr, "k_i"] & \arrow[l, phantom, "\text{isoprene}"] & \text{triplet nitrene} \arrow[d, "mk_t"] \arrow[dr, "k_t"] & \arrow[l, phantom, "\text{isoprene}"] \\
\text{II} & \text{III} & \text{II} & \text{III}
\end{tikzcd}$$

$$\frac{[\text{III}]}{[\text{II}] - [\text{III}]} = \frac{m+1}{m-1}\frac{k_s}{k_i}[\text{isoprene}] + \frac{1}{m-1} \tag{1}$$

In eq 1, II and III are the relative concentrations of the products II and III, k_s is the rate constant of addition of singlet carbethoxynitrene to either one of the double bonds of isoprene, and k_i is the rate constant of singlet to triplet change of the nitrene. The assumption is made that all-triplet nitrene leads to the formation of II or III. Therefore, k_t does not appear in eq 1. Quantitative evaluation of the data in Table II, using eq 1, is not very accurate, because of the nature of the left side of eq 1. The difference [II] − [III] is fairly small and the experimental errors given lead to a large uncertainty. Nevertheless, the predicted straight line in a plot of the left side of eq 1 *vs.* the olefin concentration is obtained with the values given in Table II. For the slope of the line, $[(m + 1)/(m - 1)][(k_s/k_i)]$, a least-squares treatment gives 0.357 ± 0.009 and the intercept $(1/(m - 1))$ is 1.72 ± 0.14. This leads to $m = 1.58 \pm 0.03$ and $k_s/k_i = 8.02$ 0.52. These values are obtained using the figures in Table II. If the extreme error limits are used (taking all positive limits for one fit and all neegative ones for the other), straight lines are also obtained. The data in Table I, for 0.5% olefin concentration, indicate that m is really about 2. In our earlier work[2] on the stereospecificity of the addition of carbethoxynitrene to *cis*- and *trans*-4-methylpentene-2, we found a k_s/k_i of 28. To compare the value for isoprene with this, we have to allow for a statistical factor of 2 (two double bonds in isoprene) so that the corrected value for the isoprene work becomes 16. Given the uncertainty introduced by the low selectivity of the triplet nitrene, and by the unknown value of $k_{s\,(4\text{-methylpentene-2})}$: $k_{s\,(\text{isoprene})}$, this is a satisfactory agreement. We conclude that the model of Scheme IV satisfactorily explains the data and carbethoxynitrene conforms to Skell's rule,[7] *i.e.*, that the singlet discriminates little between structurally different double bonds, while the triplet prefers the double bond which gives the more stable diradical intermediate.

Table I gives the data of photolytic runs. The trend toward formation of II is the same as in Table II (nitrene made by α elimination) but more II is present at all isoprene concentrations. This agrees with our earlier result.[3,33] Photolytic generation of carbethoxynitrene gives (under our conditions) about one-third of the nitrene as the triplet, while azide thermolysis and α elimination give all the nitrene as the singlet and all triplet is derived from the singlet by intersystem crossing.

Even in conformationally favorable cases, 1,4 addition was not observed. This might simply reflect the relative rate of formation of three- *vs.* five-membered rings, owing to the uniquely favorable entropy of activation for the formation of three-membered rings.[34] The ready thermal isomerization of the vinylaziridine

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II to the pyrroline XVII shows that the former is the less stable molecule, despite the conjugation of the three-membered ring with the double bond. It remains for future investigations to determine the mechanism of the ring expansion—a 1,3-sigmatropic, concerted rearrangement or a two-step radical process.

Experimental Section

Infrared and nuclear magnetic resonance spectra were obtained in carbon tetrachloride solution, using Perkin-Elmer Model 421 and Varian Model A-60 spectrometers, respectively. For the nmr spectra, tetramethylsilane was used as an internal standard. Peak shapes are noted as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Boiling points are uncorrected.

Analysis of the reaction mixtures and purification of products by gas chromatography were done on a Wilkens Aerograph Model A-90-P instrument, using the following columns: A, 1 ft × 0.25 in. 20% Ucon polar 50 HB 2000 on Anachrom ABS; B, 2 ft of the same; C, 5 ft of the same; D, 2 ft × 0.25 in. 15% Carbowax 20M on Anachrom ABS; E, 5 ft of the same. Peak areas were determined planimetrically; reproducibility was 2%. The detector response of the vpc instrument was calibrated by injection of known quantities of authentic compounds. Photochemical reactions were carried out in a Rayonet photochemical reactor (of Southern New England Ultraviolet Co.) equipped with 16 lamps emitting 84% of their energy at 2537 Å.

Reactions with Isoprene. Carbethoxynitrene by Photolysis of Ethyl Azidoformate.—Isoprene was distilled over a 75-cm packed column and the center cut, bp 33°, was used. Freshly distilled ethyl azidoformate (0.45 g, 0.004 mole) was mixed with isoprene (3.4 g, 0.05 mole) and nitrogen was bubbled through the mixture for 15 min. Irradiation at 0° for 48 hr gave a 65% yield of nitrogen; the inner wall of the irradiation tube became coated with a film of polymer. Excess isoprene and undecomposed azide were removed at room temperature and 300-mm pressure and the residue was analyzed on columns A or D at 70°. The yield of II and III was 95%, based on the nitrogen evolved.

α-Elimination Runs.—A solution of 8.7 g (0.03 mole) of N-(*p*-nitrobenzenesulfonyloxy)urethan[29] in 51 g (0.6 mole) of dichloromethane and 21 g (0.3 mole) of isoprene was deoxygenated and maintained under nitrogen at 0°. Triethylamine (3.3 g, 0.033 mole) in 9 g (0.1 mole) of dichloromethane was added slowly. After 30 min, the mixture was allowed to warm to room temperature and kept there for 2 hr. The solvent was removed at 300-mm pressure at room temperature and triethylammonium *p*-nitrobenzenesulfonate was precipitated in 90% yield by adding ether. The filtrate was again concentrated at 300 mm and the volatile products were separated by short-path distillation at 60° and 1 mm, giving a total yield of 60%. Analysis and purification was done by vpc on columns B and D.

Dilution experiments were carried out as described, keeping the molar ratio of nitrene precursor to olefin at 1:10 and using dichloromethane as the diluent. Since dichloromethane slowly produced HCl during irradiation, photolyses were run for only 2 hr. For the quantitative determination of the products from α-elimination runs, the crude reaction mixture was injected directly into the vpc apparatus, to avoid fractionation by a preceding short-path distillation.

Competition of Isoprene and Cyclohexene for Carbethoxynitrene.—A mixture of cyclohexene and isoprene, in a 2:1 molar ratio, containing 0.1 mole of ethyl azidoformate per mole of olefin (double bond) was irradiated as above and analyzed on column D at 70°. The peak areas in the vpc trace of isoprene products were 1.6 times that of the peak area of the cyclohexene addition product, 7-carbethoxy-7-azabicyclo[4.1.0]heptane. The same ratio was found when the reaction was run at about 10% mole olefin in dichloromethane.

Preparation of N-Carbethoxy-2-methyl-2-vinylaziridine (II). Isoprene 1,2-Oxide (IV).—To a slurry of N-bromosuccinimide (89 g, 0.5 mole) in dioxane (100 ml) and isoprene (34 g, 0.5 mole) was added at 0° a precooled solution of 25 ml of sulfuric acid in 100 ml of water. After stirring at room temperature for 1 hr, the mixture was diluted with three times its volume of water, the organic layer was separated, and the water phase was extracted twice with 100-ml portions of ether. The combined organic layers were washed with water and dried; the solvents were removed to leave 40 g of a residue. This was treated with a solution of 40 g (0.7 mole) of potassium hydroxide in 50 ml of water and distilled. The fraction boiling between 70 and 90° was dried and redistilled: bp 79–80°; n^{22}D 1.4150; yield, 10 g (25%). Petrov[25] gives n^{20}D 1.4142, bp 78.5–79°. The infrared spectrum showed bands at 3095, 3040, and 1640 cm^{-1}. The nmr spectrum had signals at δ 1.37 (s, 3 H), 2.58 and 2.63 (s, 2 H) (ring CH_2), 5.0–5.7 (m, 3 H) (vinyl group).

4-Amino-3-hydroxy-3-methyl-1-butene (V) was prepared analogous to Ettlinger's method.[35] To 450 ml (7.4 moles) of 28% aqueous ammonia was added at 0° during 20 min isoprene 1,2-oxide (IV) (10 g, 0.15 mole). The mixture was kept overnight in the refrigerator and for 24 hr at room temperature, then concentrated through a Vigreux column at 20 mm on a steam bath. Fractionation of the residue gave 4 g (26%) of V: bp 75–77° (12 mm); n^{24}D 1.4692. The infrared spectrum (neat) showed bands at 3600–3100, 3095, 3015, 1645, and 1600 cm^{-1}. The nmr spectrum showed signals at δ 1.17 (s, 3 H, methyl), 2.50 (s, 2 H, CH_2), 2.75–2.82 (broad, 3 H, –OH and –NH_2), 4.9–5.4 (m, 2 H, $=CH_2$), 5.5–6.0 (q, 1 H, =CH–).

Anal. Calcd for $C_5H_{11}NO$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.21; H, 10.86; N, 13.62.

2-Methyl-2-vinylaziridine (VI) was prepared following the method of Paris and Fanta[36] for the preparation of cyclohexenimine. From 5.0 g (0.05 mole) of V we obtained VI in about 10% yield. After purification by vpc on column E, the product had $n^{22.5}$D 1.4610; bp 110°; infrared spectrum, bands at 3400, 3270, 3100, 3070, and 1640 cm^{-1}; nmr spectrum, δ 1.26 (s, 3 H, –CH_3), 1.25 (s, 1 H, –NH), 1.62 and 1.65 (broad, 2 H, ring CH_2), 4.8–5.5 (m, 3 H, –$CH=CH_2$).

Anal. Calcd for C_5H_9N: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.01; H, 10.87; N, 16.70.

N-Carbethoxy-2-methyl-2-vinylaziridine (II).—To a stirred solution of 170 mg (0.002 mole) of VI and 200 mg (0.002 mole) of triethylamine in 2 ml of ether was added at 0° 216 mg (0.002 mole) of ethyl chloroformate in 1 ml of ether. After 30 min at 0° and 15 min at room temperature, the solution was filtered and the solvent was evaporated. Vpc analysis of the residue on column A at 70° showed a single peak, of the retention time of one of the products from isoprene and carbethoxynitrene. Comparison of the infrared and nmr spectra further proved the identity of the two samples: bp 60° (1 mm); n^{25}D 1.4510; infrared spectrum bands at 3100, 3070, 1720, and 1640 cm^{-1}; nmr spectrum signals at δ 1.07 and 4.93 (t, 3 H and q, 2 H, $J = 7$ Hz; –OCH_2CH_3), 1.12 (s, 3 H, –CH_3), 2.05 (s, 2 H, ring CH_2), 4.80–5.40 (m, 3 H, –$CH=CH_2$).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.43; N, 9.02. Found: C, 61.77; H, 8.51; N, 8.95.

N-Carbethoxy-2-isopropenylaziridine (III), isolated from the reactions of isoprene with carbethoxynitrene, had the following physical properties: bp 60° (1 mm); n^{25}D 1.4540; infrared spectrum, bands at 3085, 1720, and 1640 cm^{-1}; nmr spectrum, signals at δ 1.23 and 4.07 (t, 3 H and q, 2 H, $J = 7$ Hz; –OCH_2-CH_3), 1.64 (t, 3 H, typical long-range splitting of the isopropenyl CH_3, $J = 1$ Hz), 2.07 and 2.33 (m, 2 H, ring CH_2), 2.90 (d, d, 1 H, ring CH), 4.90 (m, 2 H, $=CH_2$).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.43; N, 9.02. Found: C, 61.68; H, 8.44; N, 9.10.

Reduction of III.—Conversion of III into N-carbethoxy-2-isopropylaziridine (VII) could not be accomplished by catalytic hydrogenation, but by diimide reduction. Dipotassium azodiformate[37] (400 mg, twofold excess) and III (155 mg, 0.001 mole) were stirred in methanol (2 ml) at room temperature and glacial acetic acid (120 mg, 0.002 mole) in 0.5 ml of methanol was added. After 8 hr at room temperature, the bright yellow color faded. Isolation of the reduced product by vpc at column A at 80° gave a fraction whose retention time and infrared and nmr spectra were identical with those of synthetic VII.

N-Carbethoxy-2-isopropylaziridine (VII) was prepared by the method of Hassner and Heathcock.[28] Starting with 3-methylbutene-1, the iodourethan was obtained in 44% yield as a crude product of very poor stability. Immediate treatment with potassium *t*-butoxide in *t*-butyl alcohol gave the desired VII in 45% yield: bp 78–79° (5 mm); n^{23}D 1.4384; infrared carbonyl absorption at 1725 cm^{-1}; nmr spectrum, signals at δ 0.88,

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0.98, and 1.08 (d, d, J = 5 Hz, 6 H, C(CH$_3$)$_2$), 1.23 and 4.04 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$CH$_3$), 1.90 and 2.85 (m, 3 H, ring CH$_2$ and ring CH), isopropyl CH buried under the O-ethyl CH$_3$.

Anal. Calcd for C$_8$H$_{15}$NO$_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.25; H, 9.61; N, 8.87.

2-Ethoxy-5-methyl-5-vinyl-2-oxazoline (VIII).—Ethyl orthocarbonate (2 g, 0.015 mole) and V (1.0 g, 0.01 mole) were heated to reflux with a catalytic amount of ammonium chloride for 10 min. Distillation over a Vigreux column gave about 1 g (70% yield) of ethanol and vpc on column A at 90° gave VIII in 10% yield. Its retention time and infrared and nmr spectra were identical with those obtained from carbethoxynitrene and isoprene: infrared spectrum, bands at 3108 and 1662 cm^{-1}; nmr spectrum, signals at δ 1.05 (s, 3 H, 5-methyl), 1.28 and 4.20 (t, 3 H and q, J = 7 Hz, -OCH$_2$CH$_3$), 3.47 and 3.50 (s, s, 2 H, ring CH$_2$), 4.9–5.1 (m, 2 H, =CH$_2$), 5.7–6.3 (m, 1 H, =CH–).

Anal. Calcd for C$_8$H$_{13}$NO$_2$: C, 61.91; H, 8.43; N, 9.02. Found: C, 61.89; H, 8.45; N, 8.82.

Reaction mixtures from α-elimination runs with isoprene gave VIII upon vpc on column D.

N-Carbethoxy-3-methylpyrroline (XVII) was formed from II by vpc on columns A or D at 100°: bp 60° (1 mm); infrared spectrum, bands at 3075, 1700, and 1665 cm^{-1}; nmr spectrum, signals at δ 1.25 and 4.02 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$-CH$_3$), 1.75 (s, broad, 3 Hz half-width; 3-methyl), 4.00 (m, 4 H, ring -CH$_2$), 5.4 (broad, 1 H, olefinic CH). The compound could be reduced to XVIII by hydrogenating 321 mg (0.0021 mole) in 2.5 ml of methanol in the presence of 5% palladium on charcoal. The theoretical volume of hydrogen was taken up and the product was identical in all respects with synthetic XVIII.

N-Carbethoxy-3-methylpyrrolidine (XVIII).—Ethyl chloroformate (1.5 g, 0.013 mole) in ether (2 ml) was added to 3-methylpyrrolidine[38] in 5 ml of ether at 0°. After warming slowly to room temperature, the lower (hydrochloride) layer was discarded and the ether layer was washed with 20 ml of water and dried. After removal of the solvent, the product was separated by vpc on column D: bp 75–78° (5 mm); infrared absorption of the carbonyl (neat) at 1700 cm^{-1}; nmr spectrum, signals at δ 1.05 (d, 3 H, J = 5.5 Hz, 3-methyl), 1.21 and 4.05 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$CH$_3$), 1.4–2.5 (m, 3 H, CH$_2$ at 4 and CH at 3), 2.6–3.8 (m, 4 H, CH$_2$ at 2 and 5).

Anal. Calcd for C$_8$H$_{15}$NO$_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.98; H, 9.68; N, 8.77.

Addition of Carbethoxynitrene to Cyclopentadiene.—Cyclopentadiene was prepared by cracking dicyclopentadiene and the product of bp 40–42° was used immediately. The nitrene was generated by α elimination, in dichloromethane solution, and the procedure was entirely analogous to that described for isoprene. At 13 mole % of cyclopentadiene, the yield of triethylammonium *p*-nitrobenzenesulfonate was 90%, that of volatile products, bp 45–55° (1 mm), was about 30%. Experiments at lower cyclopentadiene concentration did not give any new products. The products were separated by vpc on columns B or D. Aziridine X had a longer retention time than oxazoline XI. Aziridine X developed a red color on standing and could be converted into XI by vpc on a vpc apparatus that had been used previously to separate the crude (undistilled) reaction mixture from α-elimination runs. The properties of **N-carbethoxy-6-azabicyclo[3.1.0]hex-2-ene (X)** were infrared spectrum (neat), bands at 3050, 1715, and 1630 cm^{-1}; nmr spectrum, signals at δ 1.17 and 3.97 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$CH$_3$), 2.4–3.4 (m, 4 H, ring CH$_2$ and CH at position 1 and 5), 5.6–6.2 (m, 2 H, olefinic CH's). The first vpc fraction, **2-ethoxy-1-oxa-3-azabicyclo[3.3.0]octa-2,6-diene (XI)**, had infrared bands (neat) at 3060, 1650, and 1610 cm^{-1}. The nmr spectrum showed signals at δ 1.20 and 4.09 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$-CH$_3$), 2.45 (m, 2 H, ring CH$_2$), 4.50 (m, 1 H, ring CH next to N), 5.30 (m, 1 H, ring CH next to O), 5.70 and 5.90 (m, 2 H, olefinic CHs).

Anal. Calcd for CH$_{11}$NO$_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.70; H, 7.30; N, 9.22.

Addition of Carbethoxynitrene to 1,3-Cyclohexadiene.—Carboethoxynitrene was generated by α elimination in dichloromethane solutions of 1,3-cyclohexadiene (4 mole %) as above. A 20% yield of volatile products, bp 70–80° (1 mm), was obtained. Ethyl carbamate was identified by its infrared spectrum and retention time. The second vpc fraction was assigned the structure of **2-ethoxy-1-oxa-3-azabicyclo[4.3.0]nona-2,7-diene (XV)** on the basis of its spectra. The infrared spectrum showed bands at 3050 and 1660 cm^{-1}. The nmr spectrum showed signals at δ 1.13 and 4.16 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$CH$_3$), 1.5–2.2 (m, 4 H, ring CH$_2$), 3.8–4.1 (m, 1 H, CH–N=), 4.7–5.0 (m, 1 H, CH–O–), 5.5–6.2 (m, 2 H, olefin CH).

Anal. Calcd for C$_9$H$_{13}$NO$_2$: C, 64.65; H, 7.83; N, 8.38. Found: C, 64.90; H, 8.01; N, 8.58.

The third vpc fraction was identified as **N-carbethoxy-7-azabicyclo[4.1.0]hept-1-ene (XIV)** because it could be converted into XV by injecting it into a vpc apparatus previously used to separate the crude α-elimination reaction mixture and because of its spectral properties. The infrared spectrum showed bands at 3050, 1725, and 1630 cm^{-1}. The nmr spectrum exhibited signals at δ 1.13 and 4.05 (t, 3 H, and q, 2 H, J = 7 Hz, -OCH$_2$-CH$_3$), 1.5–3.0 (m, 6 H, ring CH$_2$ and bridgehead CH), 5.7–6.1 (m, 2 H, olefinic CH).

Anal. Calcd for C$_9$H$_{13}$NO$_2$: C, 64.64; H, 7.83; N, 8.38. Found: C, 62.01; H, 7.92; N, 8.07.

When kept at room temperature, XIV turned dark red within days. The fourth vpc fraction was assigned the structure of **5-carbethoxyamino-1,3-cyclohexadiene (XVI)** on the basis of its composition and spectral properties. The ultraviolet spectrum showed an absorption maximum at 256 mμ (ϵ 6000); the infrared spectrum (neat) had bands at 3330, 3050, 1700, and 1520 cm^{-1}. The nmr spectrum showed signals at δ 1.20 and 4.01 (t, 3 H and q, 2 H, J = 7 Hz, -OCH$_2$CH$_3$), 2.30 and 2.45 (m, m, 2 H ring CH$_2$), 4.10–4.40 (m, 1 H, allylic CH–N), 5.40–6.0 (complex, 5 H, olefinic CH and NH).

Anal. Calcd for C$_9$H$_{13}$NO$_2$: C, 64.65; H, 7.83; N, 8.38. Found: C, 63.18; H, 7.82; N, 8.23.

Registry No.—II, 15158-19-7; III, 15158-20-0; IV, 1838-94-4; V, 15158-22-2; VI, 15158-23-3; VII, 15158-24-4; VIII, 15158-25-5; X, 15158-26-6; XI, 15158-32-4; XIV, 15158-27-7; XV, 15158-28-8; XVI, 15158-29-9; XVII, 15158-30-2; XVIII, 15158-31-3; carbethoxynitrene, 2655-26-7.

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[38] F. Blicke and C.-J. Lu, *J. Am. Chem. Soc.*, **74**, 3933 (1952).